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| 14. ABSTRACT Boron is a beneficial fuel for propellants and explosives because of its high energy density. However, efficient combustion of boron particles is difficult to obtain because of an inhibiting oxide layer that covers the particles. Various metal oxides are active catalysts in graphite/carbon oxidation, but no study has been carried out to investigate metal oxides as catalysts for boron oxidation. In this paper, the effects of metal oxides on boron oxidation are introduced. The instruments used in the experiments include a thermobalance, FactSage 6.2 software, and a CO ₂ laser ignition facility. The results reveal that Bi ₂ O ₃ is the most active catalyst: it can reduce the ignition temperature by 15.2%. Fe ₂ O ₃ and SnO ₂ are the second and third most active catalysts, respectively. The other four metal oxides used in the experiments exhibit little activity on boron thermal oxidation. The catalytic action of metal oxides possibly involves the cyclic reduction of the metal oxides and the reoxidation of the resulting metals. The catalysts help transfer oxygen from the surroundings to the B-B ₂ O ₃ interface. All metal oxides used in the experiments help decrease boron ignition delay time. Two reasons are proposed to interpret the effect of metal oxides on the boron ignition delay time. | | | | | |
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Functionalization and Passivation of Boron Nanoparticles with a Hypergolic Ionic Liquid

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I. Introduction

Boron's energy density (59.0 kJ/g, 137.8 kJ/mL) is significantly higher than conventional liquid hydrocarbon fuels like gasoline and diesel (~46 kJ/g, 35-38 kJ/mL), and is greater than that of aluminum (31.0 kJ/g, 83.8 kJ/mL) or magnesium (24.0 kJ/g, 43.0 kJ/mL) [7], the most popular metal additives. Although this makes boron an attractive candidate for propulsion and high energy density fuel applications [8, 9], boron's refractory nature is a major problem in harnessing its energy content, because combustion occurs only at the boron surface. Additionally, boron oxidizes upon air exposure, creating a roughly half nanometer thick [2] layer of solid boron oxide ($T_{vap} = 1860$ °C) on the surface, which inhibits particle ignition. Reducing the boron particle size into the nanoscale substantially increases the boron surface area for combustion, and studies have shown that in the 50-200 nm size regimes, flame

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propagation and ignition rates of aluminum nanothermites increased significantly higher [10-14]. For boron particles, it has been shown that nanoboron impregnation in gel propellants results in higher combustion efficiencies [8, 15, 16] and it is expected that boron nanoparticles will behave in similar fashion [6]. Unprotected boron exposed to air is covered by a native oxide layer, which inhibits ignition and decreases the net energy density, particular for small particles where the oxide layer makes up a significant fraction of the particle mass. Therefore, generating nanoparticles that are unoxidized but still air stable has the potential to improve combustion efficiency and energy density.

Conventional methods of boron nanoparticle preparation include pyrolysis of carboranes, chemical vapor deposition, and liquid phase growth [3-6]. These methods produce high quality particles but typically use expensive reagents or are limited to small batches. For propulsion applications, the nanoparticle synthesis method should be inexpensive and readily scalable to allow cost-effective production of quantities required for fuel applications. Ball milling offers such a method, and we have previously demonstrated production of unoxidized boron nanoparticles for use in hydrocarbon fuels [1, 2]. Those particles were found to highly dispersible in jet fuel, due to the capping layer of oleic acid, which is a common capping agent for metal nanoparticle surfaces [17-19]. The polar carboxylic acid moiety binds to the metal surfaces, leaving the hydrocarbon tail group exposed, thus allowing the particles to be highly dispersible in hydrocarbon fuels and solvents. In a combustion environment, this capping layer is expected to vaporize or burn off at low temperatures, thus allowing particle ignition at much lower temperatures than oxide-coated boron.

Ionic liquids (ILs), i.e., salts with melting points below 100 °C, have been proposed as high energy density, low vapor pressure replacements for hydrazine and hydrazine derivatives in space propulsion with potential for use in monopropellant and bipropellant rocket engines [20-27] and electrospray thrusters [26, 28]. Ideally, any potential propellant should retain hypergolic properties comparable to that of hydrazine and its derivatives; thus, dicyanamide-based ILs have been seen as attractive candidates since they have shown relatively short ignition delay times compared to other known hypergolic ILs [22, 25, 29].

IL propellants have been shown to have energy densities higher than hydrazine and its derivatives. Heintz, for instance, measured a heat of combustion of 30.6 kJ/g (32.44 kJ/mL) for 1-butyl-3-methylimidazolium dicyanamide ([BMIM][DCA]) using oxygen bomb calorimetry [30], which is substantially larger than that of hydrazine (19.5 kJ/g, 19.3 kJ/mL), but still inferior to liquid hydrocarbons. An obvious strategy to improve energy density is to

incorporate materials such as boron, which have high heats of combustion. Recently, we conducted theoretical performance calculations, using the USAF AFRL propellant performance code at standard conditions, for several liquid fuels (rocket-grade kerosene, monomethylhydrazine and the IL, 1-methyl-4-amino-1,2,4-triazolium dicyanamide [MAT][DCA]) containing a concentration of 10 wt % boron particulate; and using dinitrogen tetroxide as liquid oxidizer. Notably, the boron-containing ionic liquid fuel afforded a significant improvement in theoretical volumetric impulse compared to the other fuels (i.e., 14.2 lb_f-s/in³ for the IL fuel compared to 13.3 lb_f-s/in³ for the other two fuels). Shreeve *et al.* also studied ILs with boron atoms incorporated within the IL chemical structure in the form of dicyanoborate anions [29, 31]. Although, they did not report combustion energetics, other important properties such as ignition delay, viscosity, liquidus range, thermal decomposition temperature, and vapor pressure were shown to be comparable to hypergolic ILs containing dicyanamide and nitrocyanamide anions.

Here, we focus on an alternative strategy of making oxide-free, IL-soluble boron nanoparticles as a high energy density additive for IL propellants. Specifically, we detail a milling-based method that produces boron nanoparticles that are capped with the hypergolic IL, [MAT][DCA], which has been shown previously to have a relatively short ignition delay compared to other dicyanamide based ILs [22]. Furthermore, we show that these IL-capped nanoparticles are free of boron oxide and are air stable. Finally, we note that it has recently been shown that [MAT][DCA] loaded with these boron nanoparticles remains hypergolic with no significant change in ignition delay compared to that of the neat IL, and that flame intensity and color suggest that the boron nanoparticles are burned in the hypergolic ignition test [32].

II. Experimental

Micron-sized boron powder (97%, ~2μm particles) from C.R. Supply Co. (West Hills, CA) was used as starting material. The [MAT][DCA] IL was synthesized at the Air Force Research Laboratory at Edwards AFB, as described elsewhere [33]. Two different milling procedures were studied in this experiment. In the first, [MAT][DCA] was used without any other solvents, functioning both as capping and dispersing agents for the synthesized nanoparticles. In the second, [MAT][DCA] was added to the mill as capping agent, and then diluted with acetonitrile as dispersing agent to reduce the viscosity of the mixture. The milling jars were loaded and unloaded in a nitrogen glovebox, and all liquids were degassed to remove oxygen prior to use. Furthermore, the jar was purged and filled with pressurized

Ar prior to removal from the glovebox for milling. This eliminates any possibility that N₂ gas might react with boron at local hot spots that form as the powder is being milled.

The milling in neat [MAT][DCA] was done using the same small scale shaker/mixer mill (Spex Certiprep 8000M model) that we used successfully in producing oleic acid-capped boron nanoparticles [2]. The 55-mL tungsten carbide-lined milling jar was loaded with 1.0 g of boron, together with 80.0 g of 1/8 inch tungsten carbide balls, and milled for one hour (“dry” milling). Subsequently, 10 mL of [MAT][DCA] was added, and the mixture was milled for an additional three hours. After milling, the boron/IL mixture was scraped out of the jar, and separated from the milling balls. For the process where acetonitrile was used as a solvent/dispersing agent (thus greatly reducing the required IL/boron ratio) a large planetary mill was used (Retsch, Inc. PM 400 model), together with a 500-mL tungsten carbide lined milling jar. We fabricated modified lids with two valved ports, which allow gases to be pumped out of or injected into the jar while it is in the glovebox, without opening the jar. Because this mill is much larger and generates somewhat lower collision forces [34] than the shaker mill, the milling process was modified. To compensate for the lower collision forces, the milling time was increased. Furthermore, a three step milling process was employed, comprising dry milling, ligand milling, and solvent milling steps. In the dry milling step, five grams of boron powder were dry milled with 400 grams of 1/8 inch tungsten carbide balls for 12 hours to break the feedstock to smaller particles. The mill was operated at 350 RPM, and its rotation reversed every 30 minutes with a 5-minute rest interval in between each reverse cycle. For the ligand milling step, the jar was opened in the N₂ glovebox, and 1.5 mL of [MAT][DCA] was added. The jar was resealed and the milling was resumed for three hours. The ligand milling step is intended to ensure that the freshly exposed surfaces of the boron nanoparticles interact with [MAT][DCA]. For the final solvent milling stage, the jar was again opened and 150 mL of acetonitrile was added to thin the rather viscous boron/IL mixture and allow more efficient milling and dispersion into the solvent. The solvent milling step lasted six hours. We used acetonitrile as solvent, because it is a relatively volatile polar solvent containing no oxygen. For the experiments here, we wanted to ensure that there was no possibility that unpassivated boron surfaces might react with oxygen during milling. We have also used ethanol as solvent, however, we were concerned that localized heating during the milling process might lead to some reactivity of ethanol with the unoxidized boron surfaces [35].

Safety precautions: Unpassivated boron nanoparticles are highly pyrophoric, and exposure to air leads to spontaneous ignition, which can be violent for dry particles. Ignition can occur after a delay if the particles are wet

at the time of exposure. While the goal of the milling procedures described above is to produce air-stable boron nanoparticles, as a safety measure we always treat the particles as if they were pyrophoric until they have been proven to be air-stable. All tests and characterization procedures were conducted on small quantities to minimize potential safety problems. Opening and closing of the milling jar for addition of reagents were carefully done inside a N₂ filled glovebox and, as noted, the actual milling was done in Ar. After milling, the mixture was removed from the jar inside the glove box, and a small quantity of the mixture was tested for stability by bringing it out and exposing it to air. In addition, any materials such as solvents, paper towels, sample bottles, etc. that have been in contact with boron nanoparticles must be treated as potentially pyrophoric. Before disposing such potentially contaminated items, they were exposed to air in a fume hood for several days to ensure time for oxygen to diffuse to and passivate any boron present. One additional precaution for the case of acetonitrile milling with boron is that we observed some gas build-up during milling, which was tentatively attributed to reaction of acetonitrile under milling conditions. Recognizing the possibility that such gas might contain HCN, the jar is opened inside the glovebox which was then purged and vented into a fume hood.

Scanning electron microscopy (SEM - FEI Nova Nano 600, Hillsboro, OR) and dynamic light scattering (DLS - Particle Sizing Systems NICOMP 380, Santa Barbara, CA) analysis were done to examine the particle size distributions of the samples. The composition of the samples and the oxidation state of boron was studied with X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra instrument (Chestnut Ridge, NY). XPS is only sensitive to the top few nanometers of the sample, thus it is critical that all excess IL be removed so that electrons emitted from the boron surfaces are not attenuated by inelastic scattering in the IL layer. This was done by washing the samples with ethanol. Washing was done by suspending the boron/IL mixture in ethanol, and then centrifuging the particles out of suspension, leaving the excess IL to be discarded with the supernatant ethanol. The centrifuged particles were then ultrasonicated to resuspend them in fresh solvent. This washing/centrifugation process was repeated two times to remove excess IL and ensure that the particles only retained the thin layer of IL molecules that are strongly bound to the surface. The sample was then drop-casted from ethanol solution onto a copper shim, and then dried in air for 24 hours to remove any solvent prior to introduction into the XPS instrument's vacuum system. We have previously shown that freshly cleaved boron surfaces oxidize to form the stable native oxide layer in less than a minute [2], therefore we expect that any unpassivated boron in the nanoparticle samples would be thoroughly oxidized during the washing and drying steps.

III. Results

Boron nanoparticles produced through both dry and solvent milling methods generated black suspensions. The IL-only milling produced a more viscous mixture (Fig. 1) due mainly to higher boron loading and IL content. The suspensions are stable for days and can easily be resuspended by shaking or ultrasonication, suggesting that the particles do not form strongly bound aggregates when they settle out. Figure 2 shows a representative micrograph of samples obtained from both milling processes. These samples were washed and diluted in ethanol, then drop casted onto a TEM grid, which was subsequently mounted on a SEM sample holder. Individual boron particles between 50 to 100 nm were observed in both samples. Significant aggregation was also observed, as expected, for samples prepared by drop casting and solvent evaporation. DLS analyses of both solvent-milled and ligand-milled samples are shown together in Fig. 3. The solvent milling method described above produced smaller particles, with bulk of the mass-weighted distribution in the ~25 nm range, and a small mass fraction of much larger particles around 300 and 400 nm. Ligand milling in neat [MAT][DCA] mostly generated particles in the 50 to 100 nm size range, with a small fraction (~3% of the total mass) of much larger particles at the 530 and 710 nm size range. Because different mills and milling times were used for the two processes, the origin of the size differences is not clear; however, in our previous experiences milling boron with other ligands and solvents using both mills, we find a tendency toward more efficient size reduction when a liquid solvent is used to reduce the viscosity of the milling mixture. The advantages of using liquid process control agents for size reduction have been discussed by Suryanarayana [34]. Note, however, that reactions of the solvent under milling conditions must be considered for safety reasons, as discussed above.

One of the key goals of this work was to generate boron nanoparticles that have no surface oxide layer, but are air stable under conditions that might be seen during handling and storage of boron-loaded propellants. To study the oxidation state of the boron nanoparticles we used XPS, which is a surface-sensitive technique that probes only the top ~5 nanometers of the sample. For elemental boron (i.e., B^0 - zero oxidation state), the 1s orbital binding energy is 188 eV [36]. When it is fully oxidized to B_2O_3 (i.e., B^{3+}) the 1s binding energy is shifted to 193 eV, a full 5 eV higher than in elemental boron. The top frame of Fig. 4 shows the B 1s region spectrum of boron that was solvent milled. As described above, the sample was ethanol washed and air dried prior to analysis. Note that there are large peaks present for both elemental boron (B^0) and for fully oxidized boron (B^{3+}), indicating a substantial degree of oxidation. In contrast, the bottom spectrum shows that boron particles which were milled with neat [MAT][DCA],

then washed with ethanol and air dried, shows essentially no B^{3+} peak at 193 eV. The B 1s intensity is greatly reduced in this spectrum as well, which is consistent with the boron surface retaining a significant coating of [MAT][DCA] even after thorough washing and drying. This [MAT][DCA] layer attenuates the electrons emitted from the underlying boron surfaces. The fact that the intensity is much higher in the top spectrum indicates that the boron, in addition to being partially oxidized, has much less IL on the surface, which is presumably why it is readily oxidized. In addition, the bottom spectrum shows evidence of a weak shoulder at around 191 eV which can be attributed to a partially oxidized boron species. We speculate that this shoulder results from boron atoms in the surface layer of the particles that are bound to the IL, presumably via interaction with nitrogen in the [MAT][DCA]. These results, taken together with the significant amount of nitrogen 1s signal observed in the XPS survey spectrum (Supporting information 1) demonstrates that this sample has retained a substantial passivating layer of [MAT][DCA] that is resistant to washing off, and is dense enough to exclude oxygen.

It is interesting that solvent milling the sample results in so much oxidation. This sample was milled first with neat [MAT][DCA], which presumably binds to the boron surface as it did in the ligand-milled sample. Evidently, the subsequent milling of these [MAT][DCA]-coated particles with a large excess of acetonitrile washed a substantial fraction of the [MAT][DCA] from the surface, so that the capping agent is mostly lost when the particles are centrifuged out. This removal of the [MAT][DCA] capping layer might result from the high temperature reached during milling. The jars reach temperatures $>95^{\circ}C$ during milling, and of course there may be much higher local temperatures in the energetic collisions in the jars. We also tried ethanol instead of acetonitrile in the solvent milling stage and the samples still oxidize upon washing and drying in air. Clearly, however, simply washing the samples with room temperature ethanol (bottom spectrum in Fig. 4) does not remove the IL layer, because the washed sample remains unoxidized after air drying. It appears that the boron-IL interaction is not as strong as what we have observed for the boron-oleic acid system where the oleic acid ligand remains on the particles, and protects them from subsequent oxidation even when milling is done with hexane as solvent.

One question is whether these solvent-milled particles are actually oxidized during the milling process, or if they are unoxidized after milling, but then oxidize when exposed to air prior to XPS analysis. To answer this question, we took a part of the solvent-milled sample which had not been exposed to air, washed it, and then ultrasonicated it with a 1:1 mixture of oleic acid and oleylamine, all without air exposure. We have previously found oleate to bind to boron surfaces, resulting in a capping layer that renders the particles air-stable. The particles were

then suspended in hexane, ethanol washed to remove excess capping agent, air dried, and analyzed by XPS (Supporting Information 2). The XPS of this treated sample showed minimal surface oxidation. This confirms that the boron produced by solvent milling was unoxidized, but was also unpassivated, so that oxidation occurred upon air exposure. We conclude that solvent milling, which aids in size reduction, can be used to generate unoxidized particles, as long as the capping agent is subsequently coated onto the particles before air exposure.

IV. Conclusion

This study demonstrated the efficacy of using [MAT][DCA] as a passivating ligand to produce unoxidized boron nanoparticles through ball milling techniques. [MAT][DCA]'s capability to protect boron nanoparticles from air oxidation results from the binding of the IL molecules to the surface boron atoms, and the absence of an oxide layer on the boron surfaces is expected to aid particle ignition. The details of the boron-IL interactions that result in this stable capping layer are under investigation, as the ignition properties of boron-loaded IL propellants.

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Figures

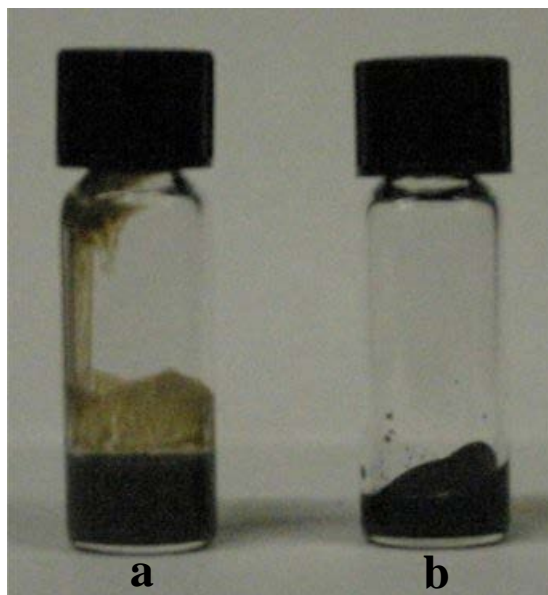


Fig. 1 Boron nanoparticles milled with (a) MAT-dca and acetonitrile as solvent, and (b) MAT-dca alone.

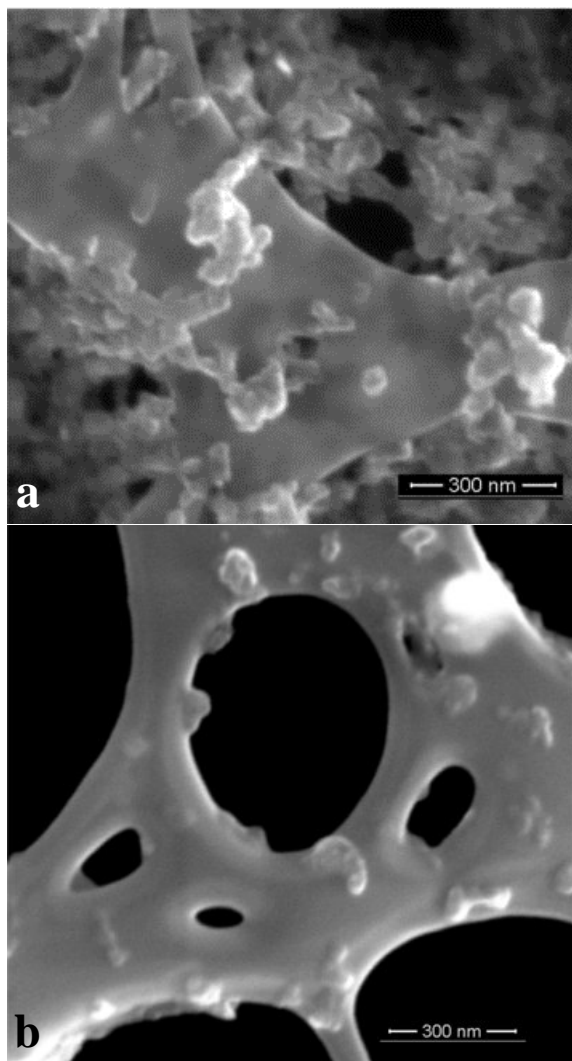


Fig. 2 SEM micrograph of boron nanoparticle samples on a TEM grid. a) Boron milled with MAT dca and acetonitrile as dispersing medium b) boron milled with MAT dca only.

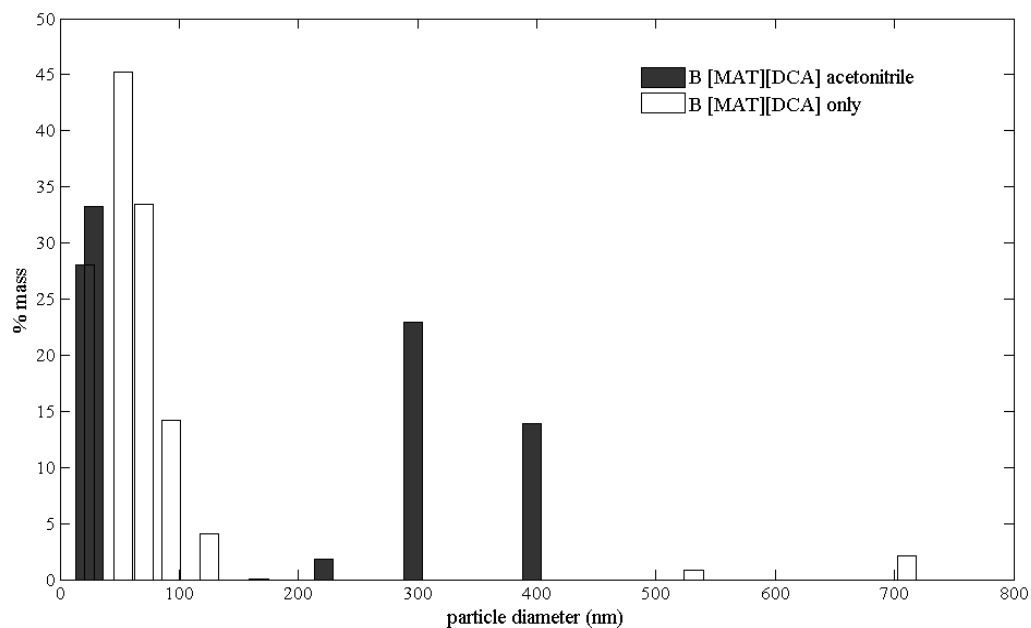


Fig. 3 DLS size distribution of boron nanoparticles from both milling processes. Milling with acetonitrile solvent produces smaller particles than by milling with MAT-dca alone.

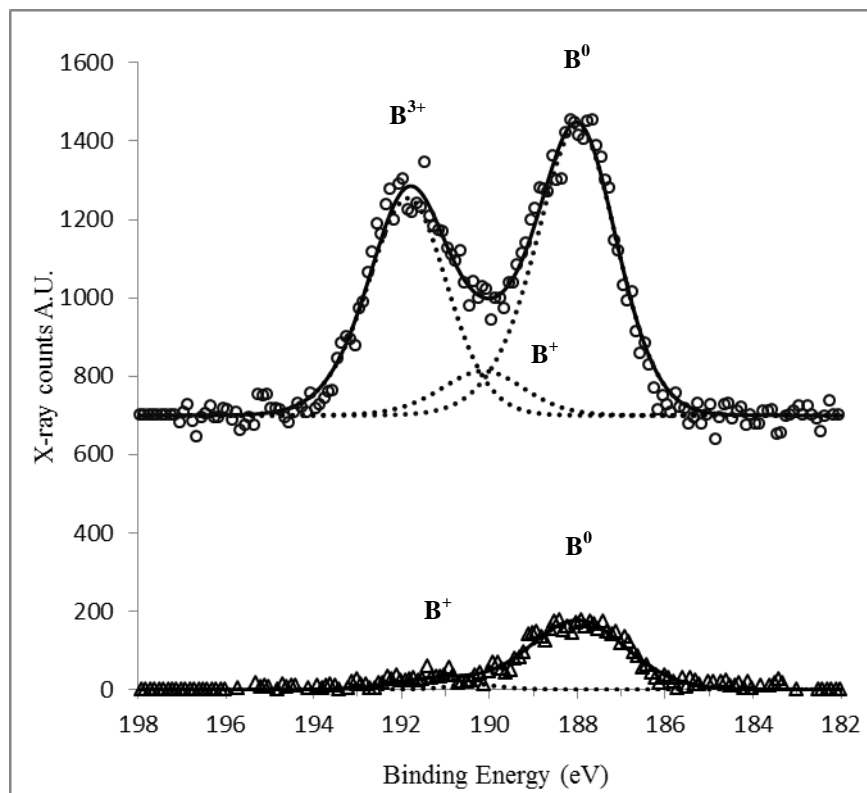


Fig. 4 High resolution Boron 1s region XP spectra of powders milled with MAT-dca and then with acetonitrile as solvent (top) and with MAT-dca only (bottom).

References

- [1] Van Devener, B., Perez, J. P. L., and Anderson, S. L., "Air-stable, unoxidized, hydrocarbon-dispersible boron nanoparticles," *J. Mater. Res.*, Vol. 24, No. 11, 2009, pp. 3462-3464.
doi: 10.1557/JMR.2009.0412
- [2] Van Devener, B., Perez, J. P. L., Jankovich, J., and Anderson, S. L., "Oxide-Free, Catalyst-Coated, Fuel-Soluble, Air-Stable Boron Nanopowder as Combined Combustion Catalyst and High Energy Density Fuel," *Energy Fuels*, Vol. 23, No. 12, 2009, pp. 6111-6120.
doi: 10.1021/ef900765h
- [3] Chakrabarti, A., Xu, T., Paulson, L. K., Krise, K. J., A.Maguire, J., and Hosmane, N. S., "Synthesis of boron nanorods by smelting non-toxic boron oxide in liquid lithium," *J. Nanomater.*, Vol. 2010, 2010, pp. 1-5.
doi: 10.1155/2010/589372
- [4] Liu, C. H., Peng, W., and Sheng, L. M., "Carbon and boron nanoparticles by pulsed-laser vaporization of boron carbide in liquids," *Letters to the editor/Carbon*, Vol. 39, 2001 pp. 137 -158.
doi: S0008-6223(00)00179-2
- [5] Pickering, A. L., Mitterbauer, C., Browning, N. D., S.M., K., and Power, P. P., "Room temperature synthesis of surface-functionalized boron nanoparticles " *Chem. Commun.*, Vol. 2007, No. 6, 2007, pp. 580-582.
- [6] Slutsky, V. G., Tsyganov, S. A., Severin, E. S., and Polenov, L. A., "Synthesis of Small-Scale Boron-Rich Nano-Size Particles," *Propell. Explos. Pyrot.*, Vol. 30, No. 4, 2005, pp. 303-309.
- [7] Cox, J. D., Wagman, D. D., and Medvedev, V. A., "CODATA Key Values for Thermodynamics." Hemisphere Publishing Corp, 1984.
- [8] Risha, G. A., Boyer, E., Evans, B., Kuo, K. K., and Malek, R., "Characterization of nano-sized particles for propulsion applications," *Materials Research Society Symposium Proceedings*, Vol. 800, 2003, pp. 243-254.
- [9] Foelsche, R. O., Burton, R. L., and Krier, H., "Boron particle ignition and combustion at 30–150 atm," *Combust. Flame*, Vol. 117, No. 1-2, 1999, pp. 32-58.
doi: 10.1016/S0010-2180(98)00080-7
- [10] Armstrong, R. W., Baschung, B., Booth, D. W., and Samirant, M., "Enhanced Propellant Combustion with Nanoparticles," *Nano Lett.*, Vol. 3, No. 2, 2003, pp. 253-255.
doi: 10.1021/nl025905k
- [11] Asay , B., Son, S. F., Busse, J. R., and Oschwald, D. M., "Ignition Characteristics of Metastable Intermolecular Composites," *Propell. Explos. Pyrot.*, Vol. 29, No. 4, 2004, pp. 216-219.

doi: 10.1002/prop.200400049

- [12] Bockmon, B. S., Pantoya, M. L., Son, S. F., Asay, B. W., and Mang, J. T., "Combustion velocities and propagation mechanisms of metastable interstitial composites," *J. Appl. Phys.*, Vol. 98, 2005, p. 064903.
doi: 0021-8979/2005/9(6)/064903/7
- [13] Plantier, K. B., Pantoya, M. L., and Gash, A. E., "Combustion wave speeds of nanocomposite Al/Fe₂O₃: the effects of Fe₂O₃ particle synthesis technique " *Combust. Flame*, Vol. 140, No. 4, 2005, pp. 299-309.
doi: 10.1016/j.combustflame.2004.10.009
- [14] Wang, L. L., Munir, Z. A., and Maximov, Y. M., "Review Thermite Reactions: Their Utilization in the Synthesis and Processing of Materials," *J. Mater. Sci.*, Vol. 28, No. 14, 1993, pp. 3693-3708.
- [15] Kuo, K. K., Risha, G. A., Evans, B. J., and Boyer, E., "Potential usage of energetic nano-sized powders for combustion and rocket propulsion.," *Materials Research Society Symposium Proceedings*. Materials Research Society, The Pennsylvania State University, 2003, pp. 3-14.
- [16] Risha, G. A. E., B. J.; Boyer, E.; Kuo, K. K., "Metals, energetic additives, and special binders used in solid fuels for hybrid rockets.," *Prog. Astronaut. Aeronaut.*, Vol. 218, 2007, pp. 413-456.
- [17] Carpenter, E. E., Calvin, S., Stroud, R. M., and Harris, V. G., "Passivated Iron as Core-Shell Nanoparticles," *Chem. Mater.*, Vol. 15, No. 17, 2003, pp. 3245-3246.
doi: 10.1021/cm034131l
- [18] Wu, N., Fu, L., Su, M., Aslam, M., Wong, K. C., and David, V. P., "Interaction of Fatty Acid Monolayers with Cobalt Nanoparticles " *Nano Lett.*, Vol. 4, No. 2, 2004, pp. 383-386.
doi: 10.1021/nl035139x
- [19] Yang, H. T., Shen., C. M., Wang, Y. G., Su, Y. K., Yang, T. Z., and H.G., G., "Stable cobalt nanoparticles passivated with oleic acid and triphenylphosphine," *Nanotechnology*, Vol. 15, No. 1, 2004, pp. 70-74.
doi: 0957-4484/04/010070+05
- [20] Jones, C. B., Haiges, R., Schroer, T., and Christe, K. O., "Oxygen-Balanced Energetic Ionic Liquid," *Angew. Chem. Int. Ed.*, Vol. 45, No. 30, 2006, pp. 4981-4984.
doi: 10.1002/anie.200600735
- [21] Schneider, S., Hawkins, T., Ahmed, Y., Rosander, M., Hudgens, L., and Mills, J., "Green Bipropellants: Hydrogen-Rich Ionic Liquids that Are Hypergolic with Hydrogen Peroxide," *Angew. Chem. Int. Ed.*, Vol. 50, No. 26, 2011, pp. 5886 – 5888.
doi: 10.1002/anie.201101751

- [22] Schneider, S., Hawkins, T., Rosander, M., Vaghjiani, G., Chambreau, S., and Drake, G., "Ionic Liquids as Hypergolic Fuels," *Energy Fuels*, Vol. 22, 2008, pp. 2871-2872.
doi: 10.1021/ef800286b
- [23] Shamshina, J. L., Smiglak, M., Drab, D. M., Parker, T. G., Dykes, J. H. W. H., Di Salvo, R., *et al.*, "Catalytic ignition of ionic liquids for propellant applications," *Chem. Commun.*, Vol. 46, No. 47, 2010, p. 8965.
doi: 10.1039/c0cc02162h
- [24] Chambreau, S. D., Schneider, S., Rosander, M., Hawkins, T., Gallegos, C. J., Pastewait, M. F., *et al.*, "Fourier Transform Infrared Studies in Hypergolic Ignition of Ionic Liquids," *J. Phys. Chem. A*, Vol. 112, 2008, pp. 7816-7824.
doi: 10.1021/jp8038175
- [25] Iyer, S., and Litzinger, T., "Reaction mechanism for hypergolic ignition of dicyanamide-based ionic liquids," *Chem. Phys. Processes Combust.*, 2009, pp. iyer1/1-iyer1/6.
- [26] Demmons, N., Roy, T., Ehrbar, E., Zwahlen, J., and Martin, R., "ST7-DRS Colloid Thruster System Development and Performance Summary," *44th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit*. AIAA, Hartford, CT, 2008, pp. 1-18.
- [27] Chiu, Y.-H., and Dressler, R. A., "Ionic liquids for space propulsion," *ACS Symp. Ser., No. Ionic Liquids IV*. Vol. 975, 2007, pp. 138-160.
- [28] Ticknor, B. W., Miller, S. W., and Chiu, Y.-H., "Mass Spectrometric Analysis of the Electrospray Plume from an Externally Wetted Tungsten Ribbon Emitter," *45th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit*. AIAA, Denver, CO, 2009, pp. 1-10.
- [29] Zhang, Y., Gao, H., Joo, Y.-H., and Shreeve, J. n. M., "Ionic Liquids as Hypergolic Fuels," *Angew. Chem. Int. Ed.*, Vol. 50, No. 41, 2011, pp. 9554-9562.
doi: 10.1002/anie.201101954
- [30] Emel'yanenko, V. N., Verevkin, S. P., and Heintz, A., "The Gaseous Enthalpy of Formation of the Ionic Liquid 1-Butyl-3-methylimidazolium Dicyanamide from Combustion Calorimetry, Vapor Pressure Measurements, and Ab Initio Calculations," *J. Am. Chem. Soc.*, Vol. 129, 2007, pp. 3930-3937.
doi: 10.1021/ja0679174
- [31] Zhang, Y., and Shreeve, J. n. M., "Dicyanoborate-Based Ionic Liquids as Hypergolic Fluids," *Angew. Chem. Int. Ed.*, Vol. 50, No. 4, 2011, pp. 935-937.
doi: 10.1002/anie.201005748
- [32] McCrary, P. D., Beasley, P. A., Cojocaru, O. A., Schneider, S., Hawkins, T. W., Perez, J. P. L., *et al.*, "Hypergolic ionic liquids to mill, suspend, and ignite boron nanoparticles," *Chem. Commun.*, Vol. 48, 2012, pp. 4311-4313.

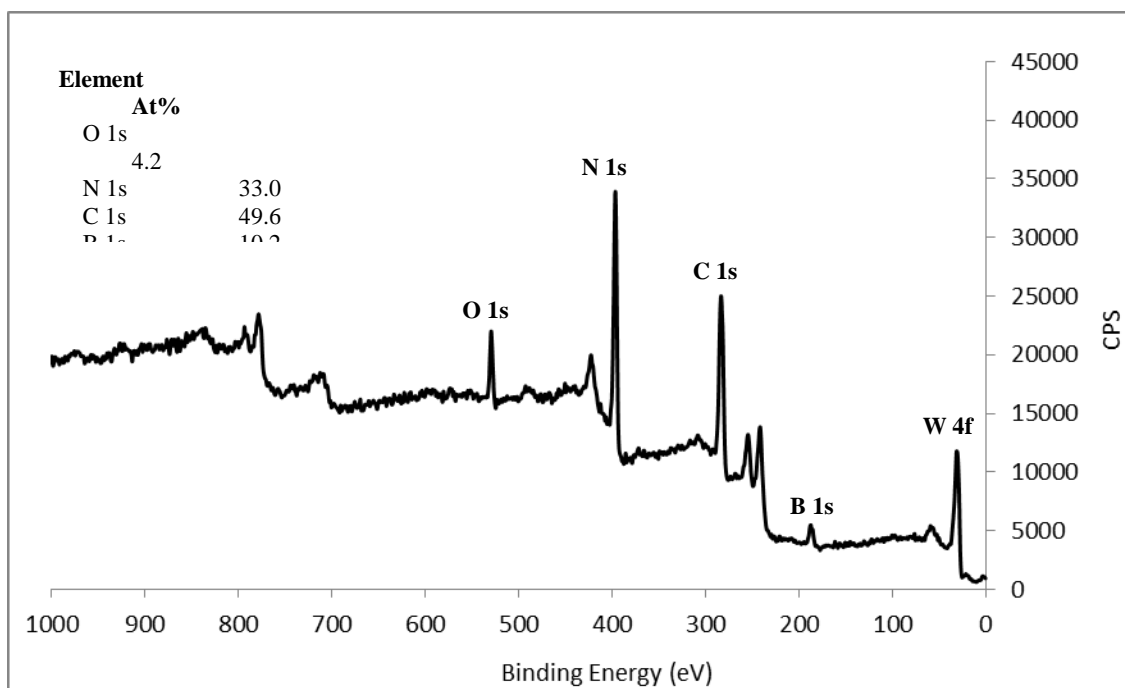
doi: 10.1039/c2cc30957b

- [33] Hawkins, T. W., Schneider, S., Drake, G. W., Vaghjiani, G., and Chambreau, S., "Hypergolic Fuels." Vol. US 8,034,202 B1, The United States of America as represented by the Secretary of the Air Force, United States, 2011.
- [34] Suryanarayana, C., "Mechanical alloying and milling," *Prog. Mater. Sci.*, Vol. 46, 2001, pp. 1-184.
- [35] DiGiuseppe, T. G., Estes, R., and Davidovits, P., "Boron Atom Reactions. 3. Rate Constants with H_2O , H_2O_2 , Alcohols and Ethers," *J. Phys. Chem.*, Vol. 86, 1982, pp. 260-262.

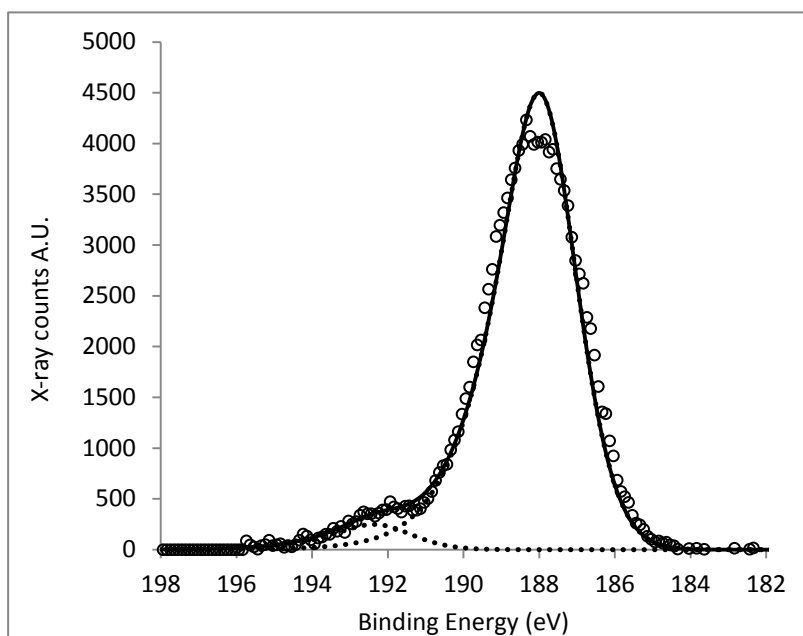
doi: 0022-3654/82/2086-0260

- [36] Moulder, J. F., Stickle, W. F., P.E., S., and Bomben, K. D., *Handbook of X-ray Photoelectron Spectroscopy*. Eden Prairie, Minnesota 55344: Perkin-Elmer Corporation, 1992.

Supporting Information



Supporting Information 1. XPS survey spectrum of a lightly sputtered boron sample milled with MAT-dca alone. Significant amount of nitrogen coming from the IL is observed even after thorough washing with ethanol.



Supporting Information 2. B 1s Region scan of B sample milled with MAT-dca and acetonitrile solvent then sonicated with oleic acid oleylamine surfactant mixture before washing and exposure to air. Oxidation is minimized by such treatment.